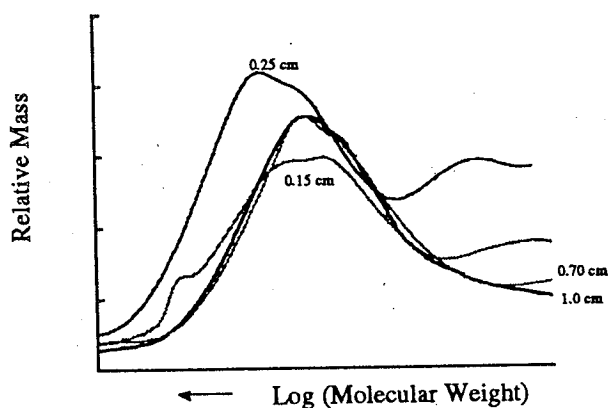
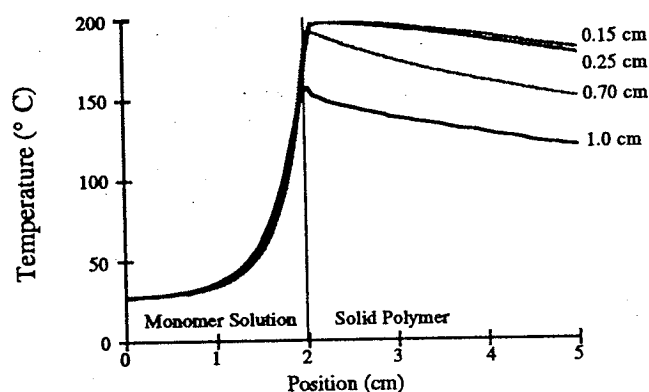
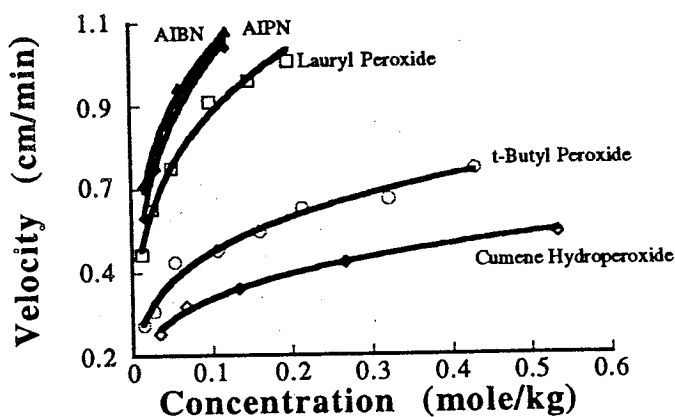


7N-27-CR  
026197**Traveling Fronts of Addition Polymerization**

John A. Pojman\*, Dionne Fortenberry, Chris E. Jones, Akhtar M. Khan, James S. Walker and Jason Willis

Department of Chemistry and Biochemistry  
University of Southern Mississippi  
Hattiesburg, MS 39406-5043

If a solution of methacrylic acid and a thermal initiator in a test tube, such as a peroxide or nitrile, is heated at the top, a solid front can be observed to propagate with a constant velocity.<sup>1-3</sup> The velocity is a function of the initiator concentration. Large thermal gradients occur along the direction of propagation and radially, with the front reaching a maximum temperature of almost 200 °C. Radial gradients of molecular weight result.

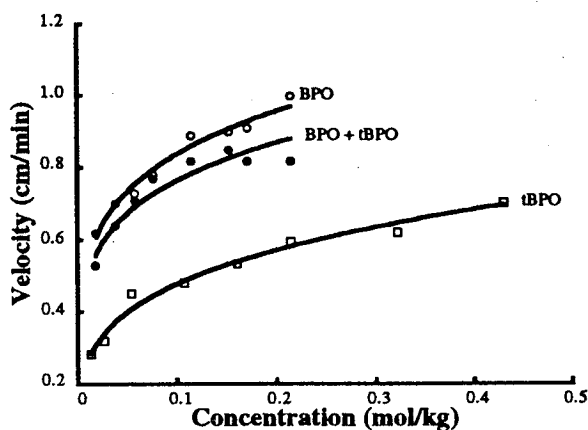
**Dual Initiator System**

From chemical analysis, we found that no more than 95% of the double bonds are reacted. If propagating fronts of polymerization are to have a practical utility, then high conversion must be achieved. A possible method to achieve this goal is to use two initiators with sufficiently different energies of activation that one initiator will only start decomposing after the first initiator. Because the front velocity is a function of initial rate, the presence of the second initiator should not affect the velocity but should increase the extent of conversion. Therefore, we investigated a dual initiator system consisting of benzoyl peroxide (BPO) and the more stable t-butyl peroxide (tBPO).

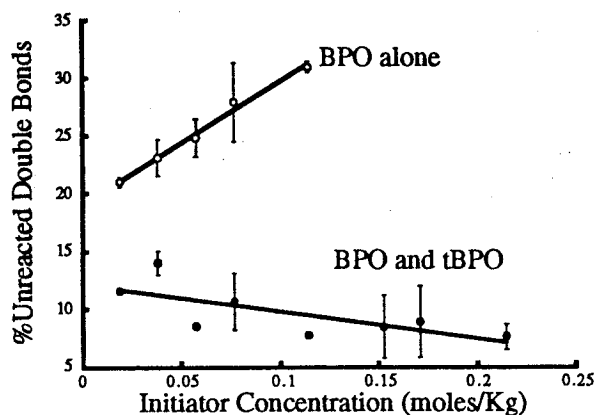
From the data in the figure below, it can be seen that the velocity dependence on initiator

concentration is not additive for the mixture of BPO and tBPO. In fact, the tBPO has a slight inhibitory effect. At 150 °C, the half-life of BPO is about 8 seconds, but the half-life of tBPO is about 1000 seconds. The slower decomposing tBPO does not contribute significantly to the initiation of polymerization. The tBPO will decompose at a significant rate after the BPO has been consumed. The degree of conversion should increase with the presence of tBPO, as indeed it does.





**BPO and tBPO Front Velocities**



**A Comparison of Front Conversion**

### Effects of Convection

Immediately under the descending front, vigorous fluid motion can be observed. Some of this is caused by bubble formation (from the initiator decomposition) during the polymerization. However, more interesting is the rolling motion of the low viscosity polymer; the radial temperature gradients cause turbulent convection.

The effect of the tube orientation with respect to the gravitational field was investigated. If the tube in which a front is propagating downward is tilted  $45^\circ$  to the vertical, the reacting solution ascends along the solid front. This material quickly forms a solid front that is perpendicular to the gravitational vector. If the tube is returned to its original orientation, the front levels off. The velocity of the front is not affected. If the tube is inverted so that the front would be propagating upward, vigorous antisymmetric convection of the unreacted solution ensues. The increased fluid motion removes sufficient heat to stop the reaction.



**A traveling front of triethylene glycol dimethacrylate polymerization in 2.2 cm diameter tube with [Benzoyl peroxide] = 1.0 g/100 mL. The tube has been tilted  $45^\circ$  to the vertical.**

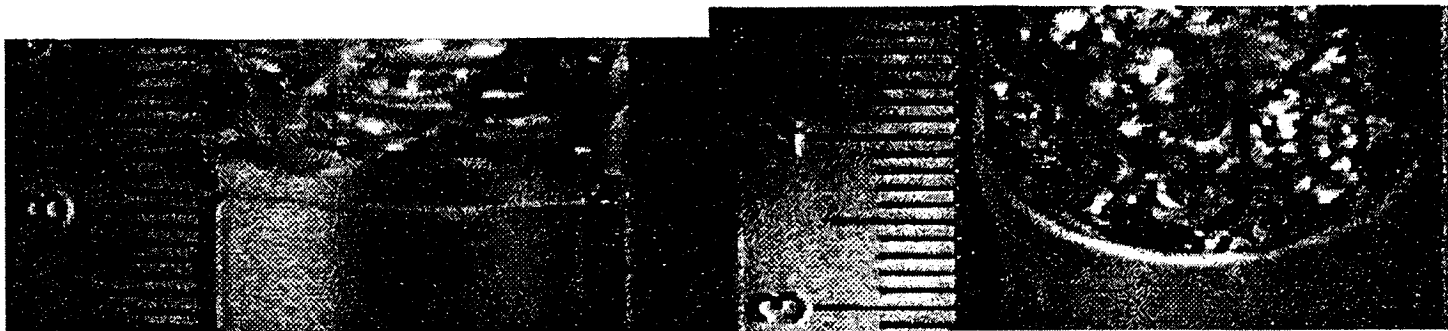
Given the large radial temperature gradients, one would expect that the front would be curved as the center regions propagated more rapidly. Nonetheless, this is not observed for normal systems. We believe that convection maintains a constant temperature across the front until the

degree of polymerization (and thus the viscosity) is high enough to prevent convection. At that point, a thermal gradient sets in, but without affecting the front velocity.

### Double-Diffusive Convection

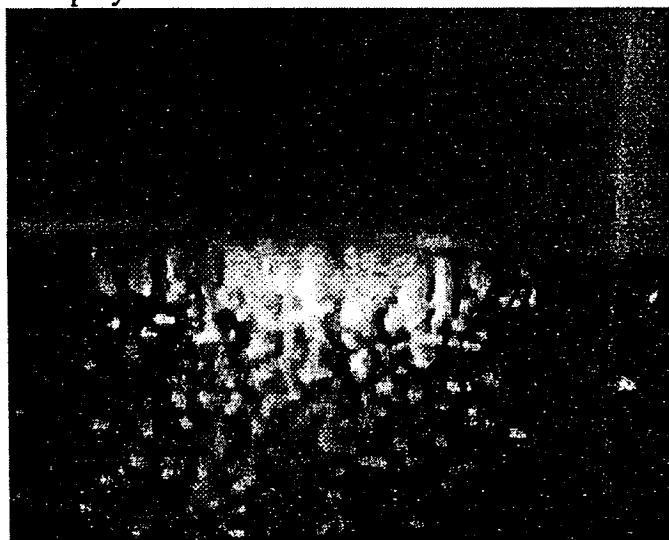
With some initiators at certain concentrations and temperatures, descending "fingers" of polymethacrylic polymer are observed that break off to form drops of solid polymer raining down the tube. Notice that the fingers occur only in a central core with BPO. Fingering never occurs with TGDMA.





Front in gelled TDGMA/benzoyl peroxide system. Front is slightly curved on the right side because of heat loss to air; it is more strongly curved on left because of heat loss to metal ruler. Front is distinctly curved when the tube is surrounded by water.

Pojman and Epstein<sup>4</sup> postulated that any exothermic traveling reaction front could cause conditions for double-diffusive (multicomponent) convection if the sum of the partial molar volumes of the products were less than the sum of the partial molar volumes of the reactants, i.e., the product solution is more dense than the reactant solution. Or, it may be thought of as having a thermal expansion ( $\Delta\rho_T < 0$ ) and an isothermal contraction ( $\Delta\rho_c > 0$ ). Free-radical polymerizations are very exothermic and form products that are more dense than the monomer. Thus, double-diffusive convection should occur in traveling fronts in a polymerization reaction.



**Fingering under a methacrylic acid polymerization front with benzoyl peroxide as the initiator. The field of view is 1.0 cm.**

Higher concentration of initiator decreases the fingering; the vigorous fluid motion at the front does not allow the formation of fingers. Very low initiator concentration also stops fingering. The low concentration of initiator may allow higher conversion and more rapid solidification of the polymer, before fingers can form.

#### **Effect of Fingering on Front Velocity**

We have observed fingering slow down the polymer fronts by as much as one third. The fingers remove heat from the front, lowering the temperature. Thus, the appearance of fingers makes it difficult to study the dependence of the front velocity on solution temperature.

Fingering can be eliminated. A viscous monomer such as TGDMA does not finger. The addition of 5% of bis-acrylamide to methacrylic acid prevents fingering. The bis-acrylamide is bifunctional and causes the viscosity of the reacting monomer solution to increase more rapidly than with methacrylic acid alone. Fingering can also be prevented by adding ultra-fine silica gel, which also increases the viscosity.

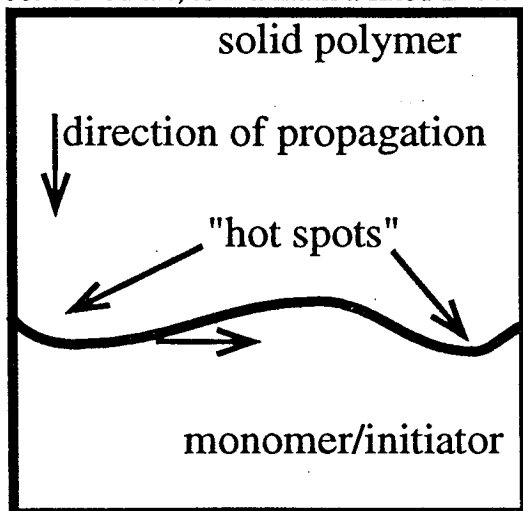
#### **Multi-dimensional Instabilities**

More complicated modes of instability can arise in cylindrical reactors. So-called "spinning" modes can arise, in which one or more hot spots (temperature maxima) are observed to propagate around the perimeter of the front. This phenomenon has been observed in solid-state combustion,<sup>5</sup> and has been studied experimentally in the  $\epsilon$ -caprolactam polymerization.<sup>6,7</sup> A schematic of a front with "hot spots." The high temperature zones are shown propagating to the right as the entire front propagates. Observed from the side, the front appears to undulate.

In studying fronts of methacrylic acid polymerization with AIBN or AIPN initiators, we have observed convection that periodically occurs under the front at the same time as the front deforms and



undulates. These reactions are performed in tubes that are exposed a continuous flow of temperature-controlled air, to maintain a fixed initial temperature and rate of heat loss.

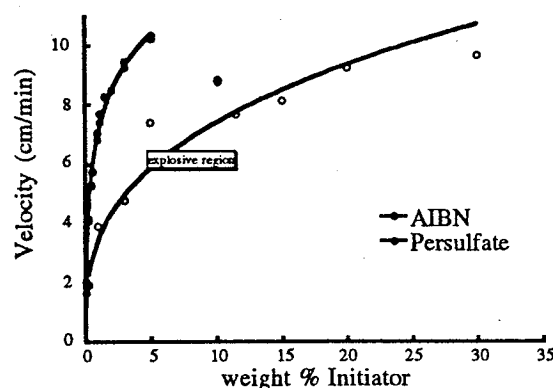
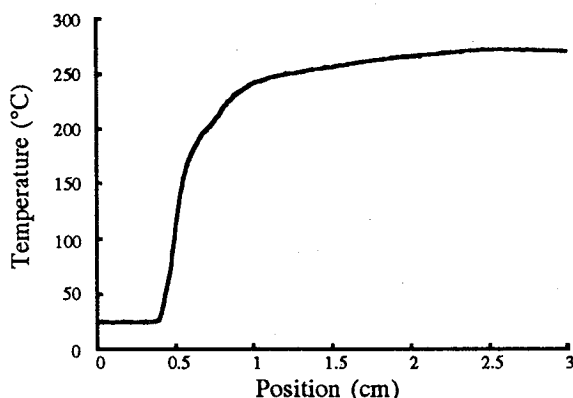


To determine if convection is essential for spinning modes, we repeated the experiment with the addition of Cabosil (ultra-fine silica gel). No convection occurred, and no spinning heads were observed.

#### Solid Fronts

We wished to study front of polymerization with solid monomers for three reasons: 1) To search for nonlinear propagation behavior. 2) To explore the possibility of a new mode of materials synthesis with reduced energy costs. 3) To study front propagation without interference from buoyancy-induced convection observed with liquid monomers.

Acrylamide and the initiator were ground in a rock tumbler with glass beads until a uniform powdered mixture was obtained (about 8 hours). The powder was packed into glass tubes, and fronts were initiated with a soldering iron. A region of solid polymer could be observed to propagate through the powdered monomer. No noticeable melt zone was observed. All reactions produced constant velocity fronts.



#### Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS for partial support of this research. We acknowledge support from the National Science Foundation's Mississippi EPSCoR Program and NASA's Microgravity Materials Science Program.

#### Literature Cited

- (1) Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284-6286.
- (2) Pojman, J. A.; Khan, A. M.; West, W. *Polym. Prepr. Am Chem. Soc. Div. Polym. Chem.* **1992**, *33*, 1188-1189.
- (3) Pojman, J. A.; Craven, R.; Khan, A.; West, W. *J. Phys. Chem.* **1992**, *96*, 7466-7472.
- (4) Pojman, J. A.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 4966-4972.
- (5) Merzhanov, A. G.; Filonenko, A. K.; Borvinskaya, I. P. *Soviet Phys. Dokl.* **1973**, *208*, 122-125.
- (6) Volpert, V. A.; Mergabova, I. N.; Davtyan, S. P.; Begishev, V. P. *Comb. Explosion and Shock Waves* **1986**, *21*, 443-447.
- (7) Begishev, V. P.; Volpert, V. A.; Davtyan, S. P.; Malkin, A. Y. *Doklady Acad. Nauk SSSR* **1985**, *279*, 909-912.
- (8) Pojman, J. A.; Nagy, I. P.; Salter, C. *J. Amer. Chem. Soc.* in press.

